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On magnetic stability of some Hamiltonians

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We investigate the magnetic stability of certain systems with Ising & Heisenberg interactions. It is found that in general the system having more number of interacting pairs is favoured most on thermodynamic considerations.

1. Introduction

Consider a set of spins, each of spin $\frac{1}{2}$, and interacting amongst themselves with a prescribed law and arranged in various geometrical shapes. The range of interaction is restricted to the nearest neighbours ; the strength is assumed to be constant. What is the most stable arrangement, in other words, which configuration will have the lowest free energy ?

Questions of similar nature were raised in the past about charged particles. For instance, Coldwell-Horsfall & Maradudin (1963) found the b.c.c. electron lattice (the one considered by Wigner, 1938) has indeed the lowest energy among b. c. c., f. c. c. and s. c. arrangements. An extensive discussion of lattice stability exists for various force laws between ionic charges (Born & Huang (1966)). These results are obviously of interest in phase transitions involving crystal structure change.

The problem for spins which we consider has, however, a serious limitation as far as physics of actual magnetic solid is concerned. The actual stability of the magnetic structure is determined only partly by the Hamiltonian that we consider and the redistribution of charge is extremely important for stability considerations. One might take the spin Hamiltonian to be an effective Hamiltonian of the solid of a particular geometrical structure. When we consider different arrangement of spins, in general the exchange constant in the Hamiltonian will not be the same as before, even though the new structure may be defined by an effective spin Hamiltonian of the old type. The exchange constant may change in several ways. If we assume the charge distribution spherical (a collection of S-state ions), the distance between nearest neighours will change or the co-ordination number itself may change, modifying the overlap integrals. The charge distribution of most magnetic ions is not spherically symmetric, hence any rearrangement of the neighbours around one ion will modify overlap integrals. Within these limitations, however, the question of stability can be discussed for some cases. The results have certain interesting features.

2. Ising hamiltonian

Take the Ising Hamiltonian first

$$H=\frac{1}{2}J\sum_{i,j}\sigma_{i\zeta}\,\sigma_{j\zeta} \qquad \ldots (1)$$

$J<0$ corresponds to the ferromagnetic case. In the two dimensional situation, the free energy per spin has been rigorously evaluated for the square, triangular and hexagonal lattices (Green & Hurst 1965, Domb 1960),

$$-f_{sq}/\kappa_B T=\frac{1}{2}\ln\sinh 2K+\frac{1}{4\pi}\int_0^{2\pi}\cosh^{-1}[\coth 2K\cosh 2K-\cos\theta]d\theta$$

$$-f_{tr}/\kappa_B T=\frac{1}{2}\ln 2+3\ln\cosh K+\frac{1}{4\pi}\int_0^{2\pi}\ln[A+\{A^2-4(1-x^2)^2X^2(\theta)\}^{1/2}]\,d\theta$$

$$-f_{hex}/\kappa_B T=-f_{tr}/\kappa_B T-\ln\cosh K-\ln(1+\tanh^3 K)+\ln 2 \qquad \ldots (2)$$

with

$$A=(1+x^2)^3+8x^3-2x(1-x^2)^2$$

$$X(\theta)=2x(1-x^2)\cos\frac{1}{2}\theta$$

$$x=\tanh K,\ K=J/\kappa_B T$$

The integrals can be numerically evaluated. We notice that for $J>0$, the triangular lattice has the lowest free energy at all temperatures. For $J<0$, the hexagonal configuration is the most favoured one. The free energy curves never cross, and no transformation from one type of lattice to another is possible.

No closed analytic expressions are available for 3-dimensions. However, series expansions for the partition function are available both in the high and low temperature limits. Domb & Sykes explicitly calculated the partition functions in powers of $\tanh(J/\kappa_B T)$ for both ferromagnetic and antiferromagnetic cases for different lattices. Focussing our attention on the simple cubic (s. c.), body centred cubic (b.c.c.) and the face centred cubic (f.c.c.) lattices, the high temperature expansions for $J<0$ (Domb 1960, Domb & Sykes 1957) :

$$s.c.\quad Z=2(\cosh K)^3[1+3w^4+22w^6+192w^8+\ldots.]$$

$$b.c.c.\quad Z=2(\cosh K)^4[1+12w^4+148w^6+2568w^8+\ldots\ldots]$$

$$f.c.c.\quad Z=2(\cosh K)^6[1+8w^3+33w^4+168w^5+\ldots..]$$

$$w=\tanh K\,;\ K=J/\kappa_B T. \qquad \ldots (3)$$

The f. c. c. lattice has the lowest free energy. For $J>0$, the f.c.c. lattice cannot be decomposed into the two sublattices, as done usually in the model of an antiferromagnet. Of the remaining lattices obviously the b. c. c. is the more stable one. Note that the right hand sides of first two equations in (3) do not depend on the sign of J. In the low temperature region Sykes *et al* (1965) give expansions for free energy for both ferromagnetic and antiferromagnetic lattices in powers of $\exp(-|J|/\kappa_B T)$. The free energy of $J<0$ is given by the formula.

$$F = -\frac{1}{2} q |J| - \kappa_B T \ln\Lambda (j, u) \qquad ...(4)$$

where ln is given by the ferromagnetic polynomials

$$s.c.\ \ln\Lambda(1,u) = u^3+3u^5-\frac{7}{2}u^6+15u^7-33u^8+\ldots\ldots,$$

$$b.c.c.\ \ln\Lambda(1,u) = u^4+4u^7-\frac{9}{2}u^8+28u^{10}+\ldots\ldots,$$

$$f.c.c.\ \ln\Lambda(1,u) = u^6+6u^{11}-\frac{13}{2}u^{12}+8u^{15}+\ldots\ldots,$$

$$u = \exp(-4|J|/\kappa_B T)$$

The dominant term at low temperatures is $-\frac{1}{2}qJ$ i. e., the free energy is asymptotically proportional to co-ordination number. Hence, the f. c. c. lattice is again the stablest configuration and the s.c. lattice has the least stability. For $J>0$ free energy is given by a formula similar to (4) but in this case $\ln\Lambda^a(1,y)$ is given by

$$s.c.\quad \ln\Lambda^a(1,y) = y^6+3y^{10}-\frac{7}{2}y^{12}+15y^{14}+\ldots\ldots$$

$$b.c.c.\quad \ln\Lambda^a(1,y) = y^8+4y^{14}-\frac{9}{2}y^{16}+\ldots\ldots$$

$$y = \exp(-4J/\kappa_B T) \qquad ...(5)$$

The b.c.c. lattice is stabler than the s. c. If we assume that as in the two dimensional situation, the free energy curves do not cross, no transition will occur from the f.c.c. to any other form in the $J<0$ case, and from b.c.c, to the s. c. in the $J>0$ case.

3. Heisenberg hamiltonian

The Hamiltonian representing the Heisenberg coupling is written as

$$H = -\frac{1}{2} J \sum_{i,j} \sigma_i \sigma_j \qquad ...(6)$$

i and j being nearest neighbours. $J>0$ corresponds to antiferromagnetic coupling. Rigorous analytical expressions for the free energy are not known for large number of particles. We shall consider what is known as the cluster problem. Here the spins are supposed to be divided into groups which do not interact with each other. Bleaney & Bowers (1954) (see also Guha 1957, Smart 1963) have discussed the case of a compound. $Cu(CH_3COO)_2.H_2O$, where a pair of Cu atoms is magnetically coupled, while different pairs are independent. We shall generalize the situation and allow each group to have 4, 6 and 8 particles, respectively. Beyond these, calculations become too involved.

Considering 4 spins first, we can arrange them at the vertices of a square (s) or a tetrahedron (t). Always allow nearest neighbour interactions. Hence the relevant Hamiltonians are

$$H_s = \frac{1}{2} J[\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_4+\sigma_4\sigma_1]$$

$$H_t = \frac{1}{2} J[\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_4+\sigma_4\sigma_1+\sigma_1\sigma_3+\sigma_2\sigma_4]. \qquad \ldots(7)$$

Taking 6 spins we may put them in the shape of a hexagonal ring (h) or at the vertices of an octahedron (o). The corresponding Hamiltonians are

$$H_h = \frac{1}{2} J \sum_{i=1}^{6} \sigma_i.\sigma_{i+1}, \ (\sigma_7 \equiv \sigma_1)$$

$$H_o = \frac{1}{2} J\Big[\sum_{i=1}^{6} \sigma_i\sigma_{i+1} + \sum_{i=1}^{6} \sigma_i.\sigma_{i+2}\Big] \qquad \ldots(8)$$

For 8 spins two structures of immediate interest are an eight member ring (r) or a cube (c)

$$H_r = \frac{1}{2} J \sum_{i=1}^{8} \sigma_i.\sigma_{i+1} \ ; \ (\sigma_9 \equiv \sigma_1),$$

$$H_c = \frac{1}{2} J[\sigma_1.\sigma_2+\sigma_2.\sigma_3+\sigma_3.\sigma_4+\sigma_4.\sigma_1+\sigma_1.\sigma_5+\sigma_2.\sigma_6$$
$$+\sigma_3.\sigma_7+\sigma_4.\sigma_8+\sigma_5.\sigma_6+\sigma_6.\sigma_7+\sigma_7.\sigma_8+\sigma_8.\sigma_5] \qquad \ldots(9)$$

We want to calculate the eigenvalues of the Hamiltonians and determine their degeneracies in order to get the free energy. The eigenvalue of the Hamiltonian in equations (7) and (8) are already available from the work of Majumdar & Ghosh (1969). They studied the effect of having next nearest neighbour interaction in a linear chain represented by the Hamiltonian

$$H = \frac{1}{2} J \sum_{i=1}^{N} \sigma_i.\sigma_{i+1} + \frac{1}{2} J_2 \sum_{i=1}^{N} \sigma_i\sigma_{i+2} \qquad \ldots(10)$$

($N+1 \equiv 1$, $N+2 \equiv 2$; $-1 \leqslant \varkappa \leqslant 1$). An essential part of their work was devoted to the study of short chains of upto ten particles. In fact it was recognized that for $\varkappa=1$, the 4 spins can be naturally arranged on a tetrahedron and six spins on an octahedron. Such arrangements could be exploited to explain the degeneracy of eigenvalues at $\varkappa=1$, because these figures have simple symmetry groups associated with them. For 8 spins the results for $\varkappa=0$ were known from Orbach (1959). The results for $\varkappa=1$ with 8 spins do not help us as there is no simple arrangement of spins in this case. We therefore diagonalized the Hamiltonian (6) for a simple cubic arrangement of spins and obtained the free energy. The eigenvalues ars listed in table 1. Dresselhaus (1962) has obtained the equations determining eigenvalues.

TABLE 1. EXCHANGE EIGENVALUES FOR A CUBIC ARRAY OF 8 ATOMS OF SPIN $\frac{1}{2}$

S_z	No. of states	Energy E/J	S_z	No. of states	Energy E/J
± 4	2	6.0000	0	2	6.0000
± 3	2	6 0000		6	4.0000
	6	4 0000		4	3.2361
	6	2.0000		2	2.5589
	2	0.0000		6	2.3402
± 2	2	6.0000		18	2.0000
	6	4 0000		6	1.2361
	4	3.2361		6	0.8284
	18	2.0000		16	0.0000
	2	0.8284		6	−0.7639
	6	0.0000		4	−1.2361
	4	−1 2361		6	−1.3778
	12	−2.0000		22	−2.0000
	2	−4.8284		2	−2.9187
± 1	2	6.0000		6	−3.2361
	6	4 0000		6	− 4.0000
	4	3.2361		6	−4.8284
	6	2.3402		6	− 4.9623
	18	2.0000		6	− 5.2361
	6	1.2361		2	− 8.0000
	2	0.8284		2	− 9.6401
	14	0.0000			
	6	− 0.7639			
	4	− 1.2361			
	6	− 1.3778			
	16	− 20000			
	6	− 3.2361			
	2	− 4.8284			
	6	− 4.9623			
	6	− 5.2361			
	2	− 8.0000			

With $J>0$, for 4 spins, at low temperature, the square, arrangement has the lowest free energy (the ground state energy per spin is of course lower) but at high temperatures the tetrahedral arrangement lies lower. The cross over occurs at $J/\kappa_B T=0.5785$. The change at this point is of the first order, in the sense that the slope of free energy changes discontinuously. The internal energy has a jump and the specific heat curve also has a finite jump.

For both 6 and 8 spin clusters with $J>0$, the 3 dimensional structures—the octahedron and the cube—lie lower in free energy than the corresponding two dimensional counter parts. The results suggest the following interprepretation. The three dimensional structures having more interparticle bonds are energetically favoured. The case of 4 spins is marginal ; the three dimensional structure allows two extra bonds, but there is not enough gain in energy (remember the coupling is antiferromagnetic). As the 3 dimensional arrangement provides more bonds the balance is tipped in favour of stability for the 3 dimensional structure. For $J<0$ it is found that in all these cases mentioned above the three dimensional structure is more stable for all regions of temperatures.

Though no closed expression for free energy for lattices with $N\to\infty$ in the Heisenberg Hamiltonian has been worked out so far, high temperature expansions in powers of $J/\kappa_B T$ are available from the work of Domb & Wood (1965). They express the zero field expansion of the partition function in the form

$$\ln Z_N(1/\kappa_B T,0)=N\ln 2+N\sum_{l=2}^{\infty} e_l (J/\kappa_B T)^l 2^l/l! \qquad \ldots (11)$$

At sufficiently high temperatures the $l=2$ term is the leading one. The coefficient e_2 has been computed by these authors to be 3/2 times the coordination number It is seen that for $J<0$, of the three lattices s.c., b. c. c. and f.c.c., the last mentioned one is the most stable and the s.c. is the least stable. For $J<0$ clearly the f. c.c. lattice, having more bonds, will be the most stable at low temperatures. Hence this is likely to be the case at all temperatures. With antiferromagnetic coupling, $J>0$, while the high temperature behaviour of the s.c. and b. c.c. lattices are given by (11), nothing exact is known about the ground state energy.

4. Discussions.

The real problem of stability which includes the geometric ordering determined almost entirely by the spin independent forces between ions and the magnetic ordering controlled by the spin dependent exchange type forces is a very hard one. However, it is thought that near the magnetic transition temperature the dominant contribution to free energy determining the magnetic structure comes from the Hamiltonian of the form

discussed in this paper. Also, in complex salts with complex geometric structures, there are only a few magnetic ions and these determine the magnetic structure of the system entirely. Such systems are also described by effective spin Hamiltonians of the Heisenberg type, and our results may have relevance to them.

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